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IDENTIFICATION (OR OTHERWISE) OF MARTIAN CARBON IN MARTIAN METEORITES. Monica M. Grady^{1,2}, V. K. Pearson¹, I. Gilmour¹, M. A. Gilmour¹, A. B. Verchovsky¹, J. Watson¹ and I. P. Wright¹; ¹PSSRI, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK, ²Dept. Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK. Contact: m.m.grady@open.ac.uk.

Introduction: One of the goals of current martian exploration is to search for evidence of extinct (or even extant) life. In recent years, this goal has been interpreted as a search for evidence of water on Mars' surface. The success of instrumentation (high resolution cameras and infrared spectrometers) on orbiting spacecraft, coupled with *in situ* data from the MER rovers have revolutionized our understanding of the surface of Mars, the type of rocks and minerals present, and their stratigraphy [1 and subsequent papers]. It is clear that there has been extensive and intensive aqueous action at different periods in Mars' history, and evidence for water is, to all intents and purposes, irrefutable. It is now time to define the next phase in the search for life as a search for regions of habitability on Mars [2]. A search for life could also be seen as a search for carbon, as one of the major assumptions that has been made in the search for life on Mars is that any life present is likely to be carbon-based.

To date, there have been no unambiguous measurements of carbon on Mars' surface. Data from the *Viking* labelled-release experiments were not clear [3]. Although Mars' thin atmosphere is approximately 95% carbon dioxide, and carbonate grains have been identified in dust in the atmosphere [4], predictions of vast carbonate reservoirs [5] have not been verified, and it is now thought that fluid on the surface might have been too acidic for the survival of carbonates [6]. In contrast to observations of the martian surface, measurements on martian meteorites have shown the presence of several different carbon-bearing components, including carbonates [7, 8]. We use data from martian meteorites to estimate the abundance and $\delta^{13}\text{C}$ of organic carbon, primary magmatic carbon and secondary carbonates that might be present on Mars.

Much is known about the behaviour of carbon on Earth as it cycles through the atmosphere, hydrosphere and lithosphere. The biosphere is a fourth carbon reservoir, and its presence influences the fixing and release of carbon in these reservoirs over different time-scales. The overall carbon balance is kept in equilibrium at the surface by a combination of tectonic processes (which bury carbon), volcanism (which releases it) and biology (which mediates it). In contrast, to Earth, Mars currently has no active tectonic system; neither does it possess a significant biosphere. However, these observations might not necessarily have held in the past. By constructing a carbon cycle for

Mars based on the carbon chemistry of martian meteorites, we investigate whether or not there is evidence for a martian biosphere

Analytical techniques: Three separate techniques were used to determine the abundance and isotopic composition of different carbon-bearing components in martian meteorites.

Component identification by stepped combustion.

Carbon-bearing phases are oxidized by incremental heating in an atmosphere of oxygen (stepped combustion). Following purification of the resulting CO_2 , the isotopic composition of the gas is measured by mass spectrometry [9]. An example of the type of data acquired is shown in Figure 1, with the temperature ranges shown over which different carbon-bearing components combust or decrepitate.

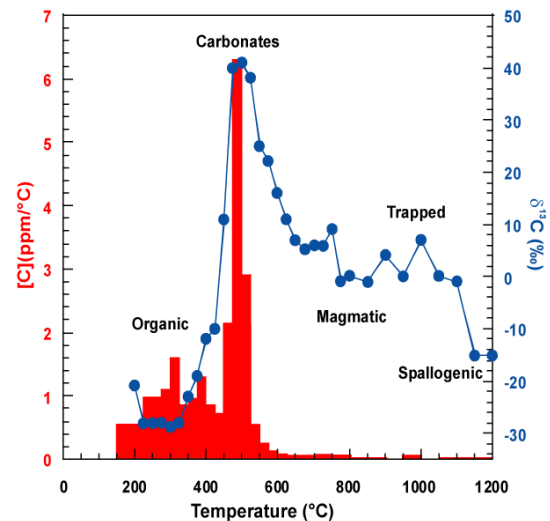
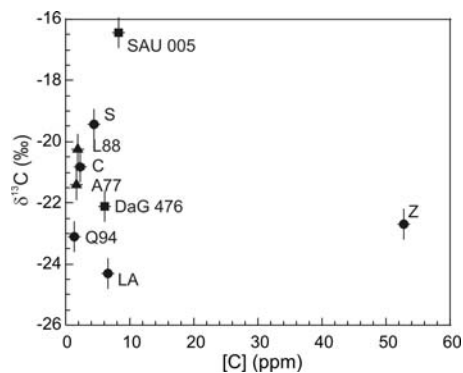


Figure 1: Results from stepped combustion of 4.5mg powdered whole rock ALH 84001. The histogram is carbon abundance in ppm/°C scaled on the left, filled circles are $\delta^{13}\text{C}$, scaled on the right. Errors in $\delta^{13}\text{C}$ are < symbol size.

We have applied this technique to Chassigny and the shergottite sub-groups of martian meteorites, in order to determine an idea of the abundance and isotopic composition of martian primary magmatic carbon [8]. These meteorites were selected because they do not seem to have experienced alteration by fluids in contact with Mars' atmosphere. Results from the study are shown in Figure 2.

Figure 2: Abundance and $\delta^{13}\text{C}$ of magmatic carbon in Chassigny and shergottites. Symbols are shergottite sub-groups: ● – basaltic; ▲ – lherzholitic; ■ – olivine-phyric.



Carbonate determination by acid dissolution.

Analysis of carbonates in martian meteorites is not easy: with the exception of ALH 84001, the carbonates are small, and generally mixed with clay minerals in cracks within primary silicates. It is difficult to analyse carbonates *in situ*, so whole rock meteorites are dissolved in 100% H_3PO_4 , following the method employed for terrestrial carbonates. However, because copious sulphur-bearing species are also generated by this procedure, there are often problems associated with producing pure CO_2 for isotopic analysis. We circumvented this problem by using a gas chromatograph to separate CO_2 from other species, prior to isotope analysis in a Thermo 253 mass spectrometer [10]. Results from analysis of 5 nakhlites are given in Figure 3.

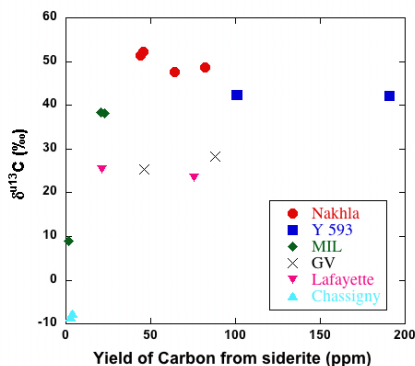


Figure 3: Results from acid dissolution of powdered whole rock nakhlites and Chassigny. Samples of between 30 – 50mg were dissolved in orthophosphoric acid at 72°C.

Organic compound identification by GC-GC-MS (4D TOFMS). A description of this technique and how it is applied to meteorites is given by [11]. Briefly, the technique employs two columns of different polarities in series. The first column, like conventional GC systems, separates compounds on the basis of molecular weight. Following this, specified fractions are passed through a second column and separated on the basis of polarity, detected by TOFMS. The system is sufficiently sensitive that only 1-2mg whole rock meteorite is required for analysis. We have used the technique to characterise organic compounds in carbonaceous chondrites

[12], and now intend to employ it to investigate organic material in martian meteorites in order to determine how much of it is terrestrial contamination and how much is non-terrestrial. Comparison of results with spectra acquired from carbonaceous meteorites will (we hope) enable us to gain an estimate of the population of organics that have been added to Mars from asteroidal and cometary impact, and that which is indigenous to Mars.

Discussion: It is clear from analysis of martian meteorites that carbon-bearing components should be detectable on the surface of Mars by suitable instrumentation. However, the most abundant species present in the igneous rocks that we analysed are carbonates, generally occurring at a level of 50 – 100 ppm. Their elevated $\delta^{13}C$ value ($\sim +50\text{‰}$) distinguishes them from terrestrial carbonates, and is presumed to result from interaction of martian atmospheric CO_2 with groundwater [10]. Magmatic carbon, released by stepped combustion of carbonate-free shergottites, generally occurs at a level of <10 ppm with $\delta^{13}C \sim -22 \pm 2\text{‰}$ [8]. Results for the organic component are in progress.

Summary: Measurement of indigenous martian carbon in martian meteorites is fraught with problems. The samples are contaminated with terrestrial organics, and the abundance of indigenous carbon is very low. Even so, we are still able to produce an inventory of carbon in martian igneous rocks, giving us a handle on the interaction between different carbon-bearing reservoirs on Mars. What is not yet clear is how carbon in the primary igneous rocks will have been transformed or removed by aqueous alteration on Mars' surface. Neither is it clear how conditions on Mars' surface will have sequestered atmospheric CO_2 into secondary clay minerals. Because the amounts of indigenous carbon are so low, it will take detailed analysis of sedimentary and igneous rocks samples returned directly from Mars before we can answer these questions.

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